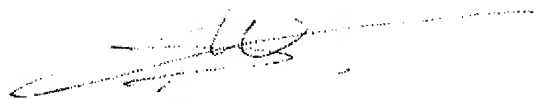


## **TRANSLATION CERTIFICATE**

I, Delphine HALIE, declare that I am suitably proficient in both English and French to translate, and hereby certify that the attached document is an accurate and complete translation of French Patent Application FR 03/04285 to the best of my knowledge, ability and belief.

**Date :** August 8, 2008

**Signatures :**



Delphine HALIE  
BREDEMA  
38 avenue de l'Opéra, F75008 (France)

## METHOD FOR THE PREPARATION OF A COMPOSITION OF NANOPARTICLES OF AT LEAST ONE CRYSTALLINE METAL OXIDE

5       The invention relates to a process for the preparation of a composition of nanoparticles of at least one crystalline metal oxide by chemical reaction of at least one organometallic precursor. It relates in particular to the preparation of a composition of dispersed nanoparticles of at least one crystalline metal oxide having at least substantially uniform  
10   forms and dimensions. It extends to novel compositions of dispersed (colloidal) nanoparticles, having at least substantially uniform forms and dimensions, of at least one crystalline metal oxide that are obtained by this process.

      In view of their specific properties which open the way for many  
15   potential industrial applications, crystalline metal oxides, especially in the form of nanoparticles, have for many years been the subject of intensive research. The document "Ceramics" Abbas Khaleel and Ryan M. Richards, Nanoscale Materials in Chemistry, Kenneth J. Klabunde, 2001, John Wiley and Sons, pp 85-120, depicts a prior art of the various methods hitherto  
20   envisaged for the preparation of nanoparticulate crystalline metal oxides, namely:

      - physical and/or aerosol methods (vapour or gas condensation; jet pyrolysis; thermochemical or flame decomposition; thermal evaporation; vaporization in vacuo; laser evaporation); these physical methods generally  
25   produce low yields, may generate undesirable products, require elevated temperatures and complex and costly apparatus;

      - chemical methods:

          • sol-gel: this method consists in carrying out the hydrolysis of precursors of the alcoholate type in water and/or an alcohol in the  
30   presence of a catalyst (an acid or base which allows the hydrolysis of the alkoxysilane to silanol or silyl ether to be accelerated, especially a mineral

acid or a mineral base such as HCl, NaOH, KOH), producing, by condensation, a gel of metal hydroxides, then, by drying of the gel, a powder, and finally, by subsequent calcination, oxides; accordingly, this method requires many successive steps including thermal treatments and generally yields only materials having a nanostructure, not well-dispersed nanoparticles;

- microemulsion: although promising, this method produces low yields and requires large quantities of solvent, a biphasic reaction and calcinations;
- chemical synthesis at low temperature in solution, and precipitation: these methods require final separating steps in vacuo and/or calcination at high temperature and do not allow the form and size of the particles to be controlled, the particles generally being undispersed;
- mechanochemical synthesis: this method does not permit the preparation of dispersed nanoparticles having uniform and predetermined forms and dimensions.

In addition, EP-0947245 describes a process for the preparation of metal colloids from an organometallic precursor ( $[\text{Sn}(\text{N}(\text{CH}_3)_2)_2]_2$  for tin) dissolved in a slightly hydrated solvent, such as anisole or commercial toluene, heating the solution, which is maintained under an inert gas, to at least 130°C in order to bring about decomposition of the precursor, and then suppressing organic by-products by at least three steps of washing with pure solvent. Nanoparticles of tin surrounded by a protective film of tin oxide are obtained. This metal colloid can be used to prepare a sensitive layer of tin oxide. To this end, a layer of metal colloid is first formed, for example by the spin-on deposition method, and is subjected to oxidation in two steps, a first step at 200°C and a second step at 650°C., and then to annealing at 450°C, to form a layer of particles of crystalline tin oxide having a diameter of 0.02  $\mu$ . In this manner there is obtained a sensitive layer of spherical agglomerated tin oxide particles.

The publications "Synthesis and characterization of monodisperse zinc and zinc-oxide nanoparticles from the organometallic precursor  $[\text{Zn}(\text{C}_6\text{H}_{11})_2]$ " F. Rataboul et al., Journal of Organometallic Chemistry 643-644 (2002) 307-312; and "New procedure towards well-dispersed nickel oxide nanoparticles of controlled size" N. Cordente et al., C. R. Acad. Sci. Paris, chimie/chemistry 4 (2001) 143-148 describe the preparation of colloids of mixed metal particles (Zn/ZnO or Ni/NiO) having a metal core and a layer of oxide, by thermal decomposition, under an inert gas, of an organometallic precursor in a manner similar to EP-0947245. The publication of F. Rataboul teaches that nanoparticles of Zn/ZnO dispersed in PVP (polyvinylpyrrolidone) can be obtained. The particles obtained in the absence of PVP, that is to say which are not dispersed, are oxidized in the air for 3 hours at 300°C. and then for 3 hours at 600°C. There is obtained a phase of nanoparticles of pure zinc oxide having a hexagonal wurtzite structure, without coalescence but not dispersed. The publication of N. Cordente et al. describes the preparation of Ni/NiO nanoparticles dispersed in PVP and indicates that preliminary tests have been carried out for the oxidation of these particles at 100°C. (below 130°C. in order to avoid decomposition of the dispersion polymer PVP) for two weeks. However, this document admits that this oxidation does not allow nanoparticles of pure NiO oxide to be obtained, even though the results obtained are considered by the authors to be promising. Nevertheless, it is found that if the oxidation treatment is sufficiently intensive to produce oxide particles, the dispersion polymer is destroyed and the oxidized particles are no longer in the dispersed state.

Accordingly, none of the known methods mentioned above permits the direct preparation of nanoparticles of pure crystalline metal oxide(s). Furthermore, none of the known methods permits the preparation of such nanoparticles in dispersed form and having homogeneous, at least substantially uniform forms and dimensions, that is to say corresponding to a unimodal distribution (distributed around a single principal mean value),

and especially substantially monodisperse (that is to say with weak dispersion around the mean value).

Moreover, most of the known methods are laborious, require complex equipment and a high level of technology and/or numerous successive steps, including thermal treatment steps and separating steps (washing, purification, etc.), produce large quantities of polluting by-products or waste (especially solvents), and are not very suitable for exploitation under profitable economic conditions on an industrial scale.

In addition, none of the known methods permits the preparation of nanoparticles of crystalline metal oxide(s) which are in dispersed form and the form of which may have form anisotropy (non-spherical), for example an elongated form (rods, threads, ribbons, etc.). In some industrial applications, however, it is important to obtain nanoparticles having uniform and controlled forms and dimensions, which are in dispersed form, and which may have form anisotropy (especially an elongated form).

Throughout this text, the following terminology is used:

- nanoparticle: any particle, whatever its form, having at least one width and a thickness that are both less than 100 nm, typically from 1 nm to 20 nm;
- organometallic precursor: any molecule or coordination compound containing at least one organic group bonded to at least one metal atom (transition metal or main group element) by a carbon atom or a hetero atom, excluding oxygen (selected especially from N, P, As, Si, S, Se, Te), of that organic group; an organometallic precursor that is spontaneously reactive to oxidation is a precursor that is converted exothermically into an oxide when it is brought into sole contact with at least one oxidizing agent such as ambient air;
- non-aqueous solvent medium: any composition capable of forming a liquid solution when it is brought into contact with at least one compound such as an organometallic precursor; this composition is non-aqueous in the sense that water does not act as a solvent agent in the composition,

which may nevertheless comprise traces of water; it may be in the liquid state initially, or alternatively it may pass into the liquid state only after contact with the compound(s) to be dissolved; it may be simple, that is to say formed of only one compound, or complex and comprise a plurality of compounds; in particular, it may comprise not only one or more compound(s) acting as solvent agent but also any other compound that is not consumed by the oxidation reaction and is substantially neutral towards the dissolution of the organometallic precursor(s) and that does or does not play a part in the oxidation reaction;

10       - colloidal liquid solution: any clear solution of solid nanoparticles dispersed in a liquid (a colloidal liquid solution diffuses light).

Within this context, the invention aims to propose a composition of at least one crystalline metal oxide, especially in the form of nanoparticles in dispersed form and having at least substantially uniform forms and dimensions, and a process for the preparation of such a composition.

15       More particularly, the invention aims also to permit the preparation of such a composition having forms and dimensions of the particles which can be predicted and controlled in a precise manner, especially which may have form anisotropy, in particular may be elongated (discs, ribbons, threads, rods, spheres, etc.). The invention aims also to permit the preparation of such a composition which may be in the form of a colloidal liquid solution.

20       The invention also aims in particular to propose an extremely simple preparation process which does not require complex apparatus, which permits the direct preparation of dispersed nanoparticles of crystalline metal oxide(s) in a small number of steps, and which is compatible with exploitation on an industrial scale under satisfactory economic conditions. The invention aims in particular to propose a process which does not involve thermal treatment and which does not produce large quantities of  
30       polluting waste.

To this end, the invention proposes a process for the preparation of a composition of nanoparticles of at least one crystalline metal oxide from at least one organometallic precursor, characterised in that:

5 - (a) precursor(s) that is(are) spontaneously reactive to oxidation is selected,

- a liquid solution of the precursor(s) in a non-aqueous solvent medium is produced,

10 - the liquid solution is brought into contact with at least one oxidizing agent under reaction conditions suitable for bringing about directly the production of nanoparticles of crystalline metal oxide(s).

The chosen reaction conditions comprise especially:

- the choice of the non-aqueous solvent medium;
- the initial concentrations;
- the reaction temperature;
- 15 - the reaction pressure.

The process of the invention accordingly consists in carrying out a chemical reaction of direct oxidation of at least one organometallic precursor in liquid solution. It differs from sol-gel processes especially in that the direct oxidation of the spontaneously reactive precursor(s), which  
20 is(are) not (an) alcoholate(s), is carried out in a non-aqueous medium, without a catalyst (such as a mineral acid or a mineral base), without passing through a step of controlled hydrolysis leading to the formation of hydroxides forming a gel (inorganic polymer) and without the need for a subsequent calcination step to obtain the oxides in the crystalline state. In  
25 a process according to the invention, the nanoparticles of crystalline metal oxide(s) are in fact obtained by simply bringing the liquid solution into contact with an oxidizing medium, without any subsequent step, especially without a calcination step.

30 The inventors have found, surprisingly, that the metal oxide in the crystalline state can be obtained directly in the form of nanoparticles without passing through metal particles, starting from an oxidized

organometallic precursor in liquid solution, provided that a precursor that is spontaneously reactive to oxidation is chosen and with suitable reaction conditions for obtaining gentle oxidation. The process according to the invention also allows the form, the homogeneity of the nanoparticles (all  
5 the same form), the size and the size distribution of the nanoparticles to be controlled, in a single step in a solvent medium.

Advantageously and according to the invention, the oxidation is carried out at ambient pressure and at a temperature of from 0°C. to 200°C.

10 In the majority of cases, it is possible to carry out the oxidation at ambient pressure and at a temperature below 50°C., especially at ambient temperature. Accordingly, the process according to the invention is extremely simple.

No clear explanation can be given by the inventors for these  
15 surprising results, which run counter to previous knowledge.

In particular, it was hitherto considered necessary, in order to obtain nanoparticles of crystalline semi-conductor materials, to pass through a composition of metal nanoparticles. In fact, crystal growth requires either reversible passage from a fluid phase (solution, melt or vapour) to the solid  
20 phase, or considerable mobility in the solid phase, in order to allow the atoms, ions and molecules to adopt positions corresponding to the development of crystal lattices. However, although a composition of purely metal nanoparticles permits the transport of atoms and coalescence phenomena within it, and behaves like a "pseudo-molten" solid, that is not  
25 the case with semi-conductor materials such as oxides, which form rigid crystal lattices that prevent such transport at low temperature. Accordingly, there was nothing to indicate that it would be possible to obtain nanoparticles of crystalline metal oxide directly.

On the contrary, the growth of semi-conductor crystals, especially of  
30 oxides, was hitherto considered to require the application of high temperatures (more than 1000°C. in the molten state or more than 500°C.



in the case of organometallic chemical vapour deposition (OMCVD) processes).

Accordingly, it was completely unforeseeable to obtain nanoparticulate crystalline metal oxide(s) simply by bringing a liquid  
5 solution of at least one organometallic precursor into contact with ambient air.

The extremely simple, inexpensive process according to the invention, in a single reaction step, accordingly acquires considerable and decisive advantages over the totality of the processes hitherto envisaged  
10 for obtaining crystalline metal oxides.

Moreover, a posteriori, the inventors have put forward the hypothesis that the surprising results obtained with the process of the invention might be explained in part by the fact that the oxidation reaction is furthered by the exothermic nature of the decomposition of the organometallic  
15 precursor. Thus, contrary to what was assumed hitherto, it is possible, in a single step, to decompose an organometallic precursor to form an oxide directly, and it would be the generation of heat from the decomposition which would allow a crystalline oxide to be obtained.

In view of the above, the process according to the invention may be  
20 employed using all elements for which there is an organometallic precursor that is spontaneously reactive to oxidation and which can be placed in a liquid solution.

Among these elements there may be mentioned: zinc, cadmium, boron, aluminum, gallium, indium, thallium, germanium, tin, titanium,  
25 zirconium, hafnium, the lanthanides (Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), scandium, yttrium, silicon, bismuth and the other transition metals.

By way of examples of organometallic precursors that are spontaneously reactive to oxidation which can be used in a process  
30 according to the invention there may be mentioned complex coordination compounds comprising at least one of the above-mentioned elements and

at least one group selected from: amides, alkyls, aryl, cyclopentadienyls, olefins, polyolefins, alkynes, alkynines, silyls.

Even more surprising is the fact that it is possible to obtain, in a selective, reproducible and quantitative manner, the crystalline metal oxide  
5 in the form of nanoparticles which are perfectly dispersed (not agglomerated) and have forms and dimensions that are at least substantially uniform, that is to say in accordance with a unimodal distribution, especially substantially homogeneous (weak dispersion), and which may even be monodisperse.

10 Furthermore, the inventors have found that the solvent medium and its structure allow the size, form and size distribution of the nanoparticles to be controlled.

To this end, advantageously and according to the invention, said solvent medium comprises at least one compound, called a ligand,  
15 selected from the Lewis bases that are able to form chemical bond -in particular covalent bond- with at least one metal atom of at least one precursor.

It has been found that it is possible precisely to vary and to control the form and dimensions of the resulting nanoparticles of oxide(s) according to  
20 the choice of the ligand(s) and the various reaction conditions employed.

Such ligands are sometimes recommended in processes for the preparation of purely metal nanoparticles. It is known that, in this case, they may affect the form of the resulting metal nanoparticles. Nevertheless, because, as indicated above, nanoparticulate crystalline metal oxides do  
25 not have the same properties of pseudo-fluidity as nanoparticulate metals, this teaching cannot be transposed in the case of the direct oxidation of the organometallic compound. In this case too, there is no clear explanation for the influence of such a ligand within the scope of the present invention. In the case of zinc, the inventors have found that an amine ligand (for  
30 example hexadecylamine) present in the liquid solution before the start of the oxidation reaction may bring about the formation of an intermediate

compound with the organometallic precursor, which intermediate compound would be attacked by the oxidizing agent and would produce forms of crystalline oxide nanoparticles different from those which would be obtained if the organometallic precursor were attacked directly by the oxidizing agent.

In the process according to the invention there is preferably used an equimolar amount of ligand(s) relative to the amount of metal atoms of the precursor(s). In other words, a stoichiometric amount of ligand(s) is used relative to the corresponding metal atoms of the precursor(s).

Advantageously and according to the invention, at least one ligand that is not volatile at the reaction temperature is chosen, this ligand acting as dispersing agent for the composition produced in the solvent medium. Accordingly, the nanoparticles of oxide(s) are spontaneously in the dispersed state (colloid) in the final composition.

The liquid solution can be left to stand in the presence of the ligand(s) under the absence of oxidizing agent for a predetermined period before the oxidation is carried out. This period may be, for example, several hours, especially of the order of from 10 hours to 20 hours.

By way of variation, the oxidation can be carried out immediately after the formation of the liquid solution. Whether or not the solution is left to stand also has an effect on the form and/or size of the resulting nanoparticles. For example, in the case of zinc oxide, without a standing period, nanoparticles of smaller dimensions are obtained.

In order to obtain elongated nanoparticles, at least one aliphatic organic compound (saturated or unsaturated), especially containing an unbranched aliphatic chain having from 6 to 20 carbon atoms, is used as ligand. Advantageously and according to the invention there is used at least one ligand selected from the group of the primary amines, thiols, phosphorus derivatives and ethers, in particular from the group comprising hexadecylamine, dodecylamine, octylamine, dodecylthiol.

Advantageously and according to the invention, the non-aqueous solvent medium is also non-alcoholic, that is to say is additionally free of any compound having reactive hydroxyl functions, in order to avoid any formation of hydroxide. In particular, the non-aqueous solvent medium is advantageously free (apart from traces) of alcohol functions and is therefore free of alcohol compound (primary, secondary to tertiary).

Advantageously and according to the invention, said solvent medium comprises at least two separate compounds. In particular, advantageously and according to the invention, said solvent medium comprises at least one ligand and at least one compound that is volatile under the reaction conditions and gradually evaporates during the oxidation. In an advantageous embodiment, said solvent medium is formed of THF and an aliphatic primary amine. The relative proportions of THF and primary amine may vary from 100%-0% to 0%-100%; depending on the chosen proportion, the form and/or size of the resulting nanoparticles of crystalline metal oxide(s) will vary.

Other compounds acting as solvent may be envisaged, for example anisole, heptane, toluene, etc. The choice depends in particular on the precursor(s) used and the metal oxide(s) formed.

In addition, it is possible according to the invention to use at least one ligand that is capable of forming a liquid solution with the precursor(s) when it is brought into contact with the precursor(s). Accordingly, the ligand(s) also act(s) as solvent agent(s) for the liquid solution, and it is not necessary to add another solvent agent specific to the solvent medium. For example, octylamine is liquid at ambient temperature. Likewise, some precursors that are in the solid state at ambient temperature and some ligands that are solid at ambient temperature, such as hexadecylamine, may form by simple mutual contact by mixing a liquid solution. Furthermore, with a ligand that is solid at ambient temperature, and if the oxidation residue(s) ("oxidation residue" means any product of the oxidation reaction other than the metal oxide(s) and the solvent medium)

is(are) volatile or solid, the composition obtained after oxidation may return spontaneously to the solid state because the precursor that forms the liquid solution with the ligand has disappeared.

Advantageously and according to the invention, each precursor is so  
5 chosen that each oxidation residue formed from that precursor is volatile under the reaction conditions. Accordingly, in a process according to the invention, the oxidation reaction produces only solid particles of metal oxide(s) and (a) volatile organic residue(s). With a volatile solvent medium, and when the oxidation residue(s) is(are) volatile, the composition resulting  
10 from the oxidation reaction is solid. It can be taken up in a different solvent medium and then forms a colloidal liquid solution.

Advantageously and according to the invention, the oxidation is carried out without stirring the liquid solution, and into contact with at least one oxidizing agent at gaseous state -in particular atmospheric air-. In  
15 particular, in an advantageous embodiment according to the invention, a volatile solvent agent and at least one organometallic precursor that forms a volatile oxidation residue are used, and the liquid solution is left in contact with ambient air without stirring. The solvent agent gradually evaporates as the air oxidizes the precursor in solution, and the oxidation  
20 residue other than the metal oxide evaporates. There is finally obtained a solid composition of metal oxide (optionally with each ligand at the surface of the nanoparticles).

Oxidizing agents other than dissolved traces of water and/or ambient air may be used, especially pure dioxygen. Nevertheless, it is an  
25 advantage of the process of the invention that the spontaneous production of nanoparticles of crystalline oxide(s) is possible simply by contact with ambient air.

Advantageously and according to the invention, zinc dicyclohexyl  $\text{Zn}(\text{C}_6\text{H}_{11})_2$ , commonly designated  $\text{ZnCy}_2$ , is chosen as precursor for the  
30 preparation of nanoparticles of crystalline zinc oxide. In the presence of hexadecylamine as ligand in an equimolar proportion with the precursor in

THF, and by carrying out the oxidation using air at ambient temperature after standing for 17 hours beforehand, a homogeneous sample of dispersed, elongated nanoparticles of crystalline zinc oxide (zincite phase) having a width of 5 nm and a length of 15 nm and having a narrow size distribution was obtained. These semi-conductor particles are also photoluminescent. Such nanoparticles which are soluble in an organic medium are of considerable practical industrial value.

Advantageously and according to the invention, the precursor tin bis(bis(dimethylamide))  $[\text{Sn}(\text{N}(\text{CH}_3)_2)_2]_2$  is chosen for the preparation of nanoparticles of crystalline tin oxide.

Advantageously and according to the invention, indium cyclopentadienyl  $\text{In}(\text{C}_5\text{H}_5)$  is chosen for the preparation of indium oxide. Advantageously and according to the invention, at least two separate precursors from the group formed by zinc dicyclohexyl  $\text{Zn}(\text{C}_6\text{H}_{11})_2$ , tin bis(bis(dimethylamide))  $[\text{Sn}(\text{N}(\text{CH}_3)_2)_2]_2$  and indium cyclopentadienyl  $\text{In}(\text{C}_5\text{H}_5)$  are chosen for the preparation of a mixed metal oxide.

The invention also relates to a composition, that can be obtained by a process according to the invention, of nanoparticles of at least one crystalline metal oxide in dispersed form, and having forms and dimensions corresponding to a unimodal distribution. No process known prior to the present invention permitted such a composition to be obtained. In particular it is not possible in practice to obtain such a composition of crystalline oxide(s) from a composition of pure or mixed dispersed metal nanoparticles.

Advantageously and according to the invention, the nanoparticles have form anisotropy (they are not spherical). Advantageously and according to the invention, the nanoparticles have an elongated form, with an average width of less than 50 nm and an average length of greater than twice the average width. Advantageously and according to the invention, the nanoparticles have an average width of from 2 nm to 7 nm and an average length of from 10 nm to 20 nm. Advantageously and according to

the invention, the composition is composed of nanoparticles of crystalline zinc oxide having a hexagonal structure free of crystalline hydroxide. Advantageously, a composition according the invention is in the form of a colloidal liquid solution.

5       The invention relates also to a process and a composition characterized in combination by all or some of the features mentioned hereinabove or appearing hereinbelow.

Further aims, features and advantages of the invention will become apparent upon reading the Examples which follow and from the  
10       accompanying figures 1 to 15, which show microscopic views of compositions according to the invention obtained in the Examples.

#### General Protocol:

15       An equimolar liquid solution of the precursor(s) and the ligand(s) is prepared under an argon atmosphere. The concentration of each starting compound in the solution is generally  $0.042 \text{ mol.l}^{-1}$ , but it may be adjusted in dependence on the size of the desired nanoparticles. The solution is left in the absence of light for a period d1 (for example 17 hours), without  
20       stirring and still under argon (without contact with an oxidizing agent). The waiting time d1 can be adjusted in dependence on the size of the desired nanoparticles. At the end of the waiting time d1 at rest, the solution is brought into contact with ambient air and ambient humidity. It remains in contact with ambient air and humidity for a period d2, which generally  
25       corresponds to the time required for the solvent to evaporate completely, when the solvent is sufficiently volatile at ambient temperature. In the case where the solvent has not evaporated completely after several days, it is noted that nanoparticles of crystalline metal oxide have formed. When the solvent is sufficiently volatile and has evaporated completely, a solid  
30       product corresponding to a sample of crystalline metal oxide is obtained. In the particular case of ZnO, when the solvent is not sufficiently volatile to

have evaporated completely, the formation of nanoparticles can be verified by irradiating the solution under UV ( $\lambda=312$  nm), the solution becoming luminescent. In general, all the colloidal liquid solutions obtained from ZnO have luminescent properties. When a solid sample is obtained, the crystalline phase obtained can be verified by powder diffraction of the sample. In the case of ZnO, the resulting diffractogram corresponds to ZnO in the hexagonal zincite phase having the space group  $P6_3mc$ . Additional diffraction peaks correspond to organic species. These species have been characterized by NMR in solution and correspond to the ligand(s) present at the surface of the particles. In the case of colloidal liquid solutions, the crystallinity of the nanoparticles can be verified by electronic diffraction of the samples deposited on the microscopy grating. In all the examples, crystalline nanoparticles have been obtained. The microscopy gratings are prepared by depositing a drop of the colloidal liquid solution on the grating. The use of transmission electron microscopy, TEM, also allows the size, form and homogeneity of the nanoparticles formed to be observed. In all the examples it has been possible to obtain colloidal liquid solutions. The surface state of the nanoparticles was studied by NMR in solution, and the presence of the ligand(s) introduced into the reaction medium was noted. In the case of amines, it has been possible to demonstrate coordination via the  $NH_2$ -function. The nanoparticles synthesised by this method formed entities which behave like any conventional chemical product and possess, for example, a concentration at saturation at which passage from a colloidal solution to a turbid suspension occurs. This concentration is intrinsic to each system. Starting from these colloidal solutions it is possible to form monolayers of nanoparticles which have a tendency to self-organisation.

#### EXAMPLE 1

In this Example, the effect of the initial concentration on the resulting nanoparticles is evaluated.



An equimolar ( $0.042 \text{ mol.l}^{-1}$ ) solution in THF of the zinc precursor,  $\text{ZnCy}_2$ , in the presence of the ligand hexadecylamine, HDA, is prepared in a Schlenck-type reactor under a controlled argon atmosphere. The solution is then left in the absence of light for 17 hours, without stirring, and then the reactor is opened and brought into contact with ambient air and humidity. When the THF has evaporated completely, a white solid is obtained. The solid can be dissolved again in several milliliters of THF, and a colloidal liquid solution is obtained. Under these conditions, nanorods having an average size of  $10 \text{ nm} \times 5 \text{ nm}$  are obtained (figure 1). When this experiment is carried out under the same conditions but with a starting solution having a precursor concentration of  $0.125 \text{ mol.l}^{-1}$ , longer nanorod(s) ( $15 \text{ nm} \times 5 \text{ nm}$ ) are obtained (figure 2).

#### EXAMPLE 2

In this Example, the effect of the chosen solvent on the resulting nanoparticles is evaluated.

The experiment of Example 1 (figure 1) is carried out under the same conditions but using toluene, heptane or anisole, respectively, in place of THF to form the starting solution. Nanosphere(s) of  $13 \text{ nm}$  (figure 3),  $7 \text{ nm}$  (figure 4) and  $14 \text{ nm}$  (figure 5), respectively, are obtained.

It is to be noted that it is also possible to use a process according to the invention in the absence of solvent either if the ligand(s) used is(are) liquid, or if bringing the precursor into contact with the ligand(s) results in the formation of a liquid solution of an intermediate complex as it has been possible to demonstrate in the case of  $\text{ZnCy}_2$  in the presence of ligand having an amine function for which it has been possible to identify a complex of the  $\text{ZnCy}_2(\text{RNH}_2)$  type by NMR. In fact, the intermediate can have a melting point such that it is liquid at ambient temperature. Under the standard concentration conditions ( $0.042 \text{ mol.l}^{-1}$ ), with  $\text{ZnCy}_2$  as precursor, and with different amines, it has been possible to synthesise nanorod(s). The length of these nanorod(s) depends on the length of the chain of the amine used as ligand. For example, in the case of HDA, nanorod(s) of  $15$

nm x 2 nm have been obtained (figure 6), while in the case of octylamine, OA, nanorod(s) of 10 nm x 3 nm have been synthesised (figure 7).

### EXAMPLE 3

In this Example, the effect of the length of the aliphatic chain of the ligand on the resulting nanoparticles is evaluated. In the case of HDA, nanorod(s) have been obtained, while nanosphere(s) have been obtained for shorter chain lengths. The ligand therefore affects the form of the nanoparticles. However, the chain length also influences the size of the nanoparticles. Accordingly, when the length of the aliphatic chain of the ligand diminishes, the size of the resulting nanosphere(s) increases.

An equimolar ( $0.042 \text{ mol.l}^{-1}$ ) solution in THF of the zinc precursor,  $\text{ZnCy}_2$ , in the presence of the ligand dodecylamine, DDA, is prepared in a Schlenk-type reactor under a controlled argon atmosphere. The solution is then left in the absence of light for 17 hours, without stirring, and then the reactor is opened and brought into contact with ambient air and humidity. When the THF has evaporated completely, a white solid is obtained. The solid can be dissolved again in several milliliters of THF, and a colloidal liquid solution is obtained. Under these conditions, nanosphere(s) having an average size of 9 nm are obtained (figure 8). This experiment is repeated under the same conditions but with octylamine, OA, as ligand. Nanosphere(s) of 12 nm are then observed (figure 9).

### EXAMPLE 4

In this Example, the effect of the resting time  $d_1$  of the starting solution under an inert argon atmosphere (before oxidation) on the resulting nanoparticles is evaluated. This parameter affects the size of the nanoparticles. In Example 1, with the  $0.042 \text{ mol.l}^{-1}$  solution and with  $d_1=17$  hours, nanorod(s) having an average size of 10 nm x 5 nm are obtained (figure 1). This experiment is repeated under the same conditions but with a resting time  $d_1$  of zero. Nanorod(s) having an average size of 16 nm x 7 nm are then obtained (figure 10).

### EXAMPLE 5

In this Example, the effect of the exposure time to ambient air and humidity on the resulting nanoparticles is evaluated. This parameter affects the homogeneity of the synthesised nanoparticles. For example, an equimolar ( $0.042 \text{ mol.l}^{-1}$ ) solution in THF of the zinc precursor,  $\text{ZnCy}_2$ , in the presence of the ligand hexadecylamine, HDA, is prepared in a Schlenk-type reactor under a controlled argon atmosphere. The solution is then left in the absence of light for 17 hours, without stirring, and then the reactor is opened and brought into contact with ambient air and humidity. At the end of 24 hours, evaporation is still not complete and the sample is composed both of 3 nm nanosphere(s) and of nanorod(s) of 5 nm x 2 nm. After 72 hours, the sample is composed solely of nanorod(s) having an average size of 15 nm x 5 nm (figure 11).

#### EXAMPLE 6

In this Example, the effect of the reaction temperature on the resulting nanoparticles is evaluated. Examples 1 to 5 yield good results at ambient temperature. In the presence of a solvent (THF), the synthesised nanoparticles are less homogeneous and have a substantially smaller average size. Under the conditions of Example 2 (figure 6) at ambient temperature, nanorod(s) having an average size of 15 nm x 2 nm are obtained. When this experiment is repeated under the same conditions but at a temperature of  $46^\circ\text{C}$ ., the sample is composed both of 5 nm nanosphere(s) and of nanorod(s) of 10 nm x 5 nm (figure 12).

#### EXAMPLE 7

In this Example, the effect of the oxidation kinetics/evaporation of the solvent on the resulting nanoparticles is evaluated. This parameter affects both the form and the size of the synthesised nanoparticles. Under the conditions of Example 1 (figure 1), nanorod(s) having an average size of 10 nm x 5 nm are obtained. When this experiment is repeated under the same conditions but equipping the reactor with a septum pierced by a cannula having a diameter of 1 mm and a length of 3 cm, both the

oxidation kinetics and the evaporation of the solvent are much slower. After two weeks in solution, 7 nm nanosphere(s) are obtained (figure 13).

#### EXAMPLE 8 : Tin Oxide

An equimolar ( $0.042 \text{ mol.l}^{-1}$ ) solution in THF of the zinc precursor  
5  $[\text{Sn}(\text{N}(\text{CH}_3)_2)_2]_2$  in the presence of the ligand hexadecylamine, HDA, is prepared in a Schlenck-type reactor under a controlled argon atmosphere. The solution is then left in the absence of light for 17 hours, without stirring, and then the reactor is opened and brought into contact with ambient air and humidity. When the THF has evaporated completely, a white solid is  
10 obtained. The solid can be dissolved again in several milliliters of THF, and a colloidal liquid solution is obtained. Under these conditions, crystalline nanoparticles approximately 50 nm in size and having facets are obtained (figure 14).

#### EXAMPLE 9 : Mixed Oxides

15 Mixed oxides are prepared by following the same procedure as in Example 8 using an equimolar solution in THF containing the zinc precursor,  $\text{ZnCy}_2$  ( $0.021 \text{ mol.l}^{-1}$ ) and the tin precursor,  $[\text{Sn}(\text{N}(\text{CH}_3)_2)_2]_2$  ( $0.021 \text{ mol.l}^{-1}$  in tin atom equivalents) in the presence of the ligand hexadecylamine, HDA ( $0.042 \text{ mol.l}^{-1}$ ). Under these conditions, crystalline  
20 nanoparticles less than 10 nm in size and having facets are obtained (figure 15).

**CLAIMS**

1. A process for the preparation of a composition of nanoparticles of at least one crystalline metal oxide from at least one organometallic precursor, wherein:
  - 5       - at least one organometallic precursor that is spontaneously reactive to oxidation is chosen,
  - a liquid solution of said at least one precursor in a non-aqueous solvent medium is produced,
  - said liquid solution is brought into contact with at least one oxidizing agent
  - 10     under reaction conditions chosen so as to directly bring about the production of nanoparticles of crystalline metal oxide(s).
2. The process of claim 1, wherein said solvent medium comprises at least one compound, called a ligand, selected from the group consisting of the Lewis
- 15     bases that are able to form a chemical bond with at least one metal atom of at least one precursor.
3. The process of claim 2, wherein there is chosen at least one ligand that is not volatile at the reaction temperature and that acts as dispersing agent for the
- 20     composition produced in the solvent medium.
4. The process of claim 2 or 3, wherein an aliphatic organic compound is used as ligand.
- 25     5. The process of claim 4, wherein an organic compound containing an unbranched aliphatic chain having from 6 to 20 carbon atoms is used as ligand.
6. The process of one of the claims 2 to 5, wherein at least one ligand is selected from the group consisting of the primary amines, the thiols, the
- 30     phosphorus derivatives and the ethers.
7. The process of claim 6, wherein at least one ligand is selected from the group consisting of hexadecylamine, dodecylamine, octylamine, dodecylthiol.

8. The process of one of the claims 1 to 7, wherein said solvent medium comprises at least two separate compounds.

5        9. The process of one of the claims 2 and 8, wherein said solvent medium comprises at least one ligand and at least one compound that is volatile under the reaction conditions and gradually evaporates during the oxidation.

10       10. The process of claim 9, wherein said solvent medium is formed of THF and an aliphatic primary amine.

15       11. The process of one of the claims 1 to 10, wherein the oxidation is carried out at ambient pressure and at a temperature of from 0°C. to 200°C, in particular at ambient temperature.

12. The process of one of the claims 1 to 11, wherein each precursor is chosen so that each oxidation residue formed from the precursor is volatile in the reaction conditions.

20       13. The process of one of the claims 1 to 12, wherein the oxidation is carried out without stirring the liquid solution and into contact with at least one oxidizing agent at gaseous state—in particular atmospheric air.

25       14. The process of one of the claims 1 to 13, wherein said solvent medium is non-alcoholic.

30       15. The process of one of the claims 1 to 14, wherein, for the preparation of nanoparticles of crystalline zinc oxide, zinc dicyclohexyl  $\text{Zn}(\text{C}_6\text{H}_{11})_2$  is chosen as precursor.

16. The process of one of the claims 1 to 15, wherein, for the preparation of nanoparticles of tin oxide, the tin bis(bis(dimethylamide))  $[\text{Sn}(\text{N}(\text{CH}_3)_2)_2]_2$  is chosen as precursor.

17. The process of one of the claims 1 to 16, wherein, for the preparation of indium oxide, indium cyclopentadienyl  $\text{In}(\text{C}_5\text{H}_5)$  is chosen as precursor.

5 18. The process of one of the claims 1 to 17, wherein, for the preparation of a mixed metal oxide, at least two separate precursors are chosen from the group consisting of zinc dicyclohexyl  $\text{Zn}(\text{C}_6\text{H}_{11})_2$ , tin bis(bis(dimethylamide))  $[\text{Sn}(\text{N}(\text{CH}_3)_2)_2]_2$ , indium cyclopentadienyl  $\text{In}(\text{C}_5\text{H}_5)$ .

10 19. A composition of nanoparticles of at least one crystalline metal oxide in a dispersed form and having forms and dimensions corresponding to a unimodal distribution.

20. The composition of claim 19, wherein the nanoparticles have form anisotropy.

15

21. The composition of one of the claims 19 or 20, wherein the nanoparticles have an elongated form with an average width of less than 50 nm and an average length of greater than twice the average width.

20 22. The composition of claim 21, wherein the nanoparticles have an average width of from 2 nm to 7 nm and an average length of from 10 nm to 20 nm.

23. The composition of one of the claims 19 to 22, which is composed of nanoparticles of crystalline zinc oxide having a hexagonal structure free of crystalline hydroxide.

25

24. The composition of one of the claims 19 to 23, which is in the form of a colloidal liquid solution.

08/08/2008 13:31

Serial No. 31103364

TC: 256903

Destination	Start Time	Time	Prints	Result	Note
Bresse Majerowicz	08-08 13:31	00:00 25	001/001	OK	L1

Note L1: Main Circuit, L2: Sub Circuit, TMR: Timer, POL: Poll, ORG: Original,  
FME: Frame Erase TX, MIX: Mixed Original, CALL: Manual Communication,  
CSRC: CSRC, FWD: Forward, PC: PC-FAX, BND: Bind, SP: Special Original,  
FCODE: F-Code, RTX: Re-Tx, RLY: Relay, MBX: Secure, BUL: Bulletin

Result OK: TX OK, S-OK: Stop Communication, PW-OFF: Power Switch OFF, TEL: RX from TEL,  
NG: Other Error, Cont: Continue, No Ans: No Answer, Refuse: Receipt Refused,  
Busy: Busy, M-Full: Memory Full.

0147096778

BREDEMA

19:17:09

08-08-2008

1/24



**BREDEMA**  
IP Assets Management & Strategy  
CONSEIL EN PROPRIÉTÉ INDUSTRIELLE  
EUROPEAN PATENT, TRADEMARK & DESIGN ATTORNEYS

Privileged  
and  
confidential

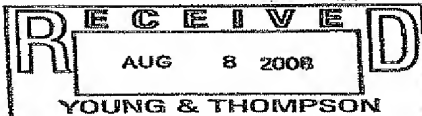
Pierre BRESE - President  
Marc BROYDE  
Jean-Benoît BUSNEL  
Anne DESMOUSSEAUX  
Amin KAISER

Eric ENDERLIN  
Guillaume NORTREUX  
Thierry SCHWARTZ

François DUSOLIER  
Elisabeth THOULET LEMAITRE

Facsimile (703-685-0573 and 703-979-4709)

YOUNG & THOMPSON  
International Patent Law  
745 South 23rd Street  
ARLINGTON VIRGINIA 22202  
USA



Paris, 08/08/2008

O/Ref: 100214/PCT/US

NLA/NTA 238555 MMV/9JB/RW

Y/Ref: 0617-1028

Re: Demande de brevet USA N° 10/551 948 en date du 06/04/2004  
METHOD FOR THE PREPARATION OF A COMPOSITION OF  
NANOPARTICLES OF AT LEAST ONE CRYSTALLINE METAL OXIDE

Dear Robert,

We write further to our facsimile correspondence of August 7th in the above-referenced case.

It has come to our attention that the "priority document" in our file was mistakenly labelled as such, and that the translation that we forwarded to you by facsimile on Aug. 7th is actually not an accurate translation of the priority document as filed. Therefore, please discard that translation.

Please find attached a revised translation with accompanying translation certificate, for submission to the USPTO.

Please acknowledge safe receipt of same by return email or facsimile.

Best regards,

Delphine HALIE

Nadège LAGNEAU